

The One-Electron Atom

I. The Schrödinger Equation for the Hydrogenic Atom

A. The Hydrogenic Hamiltonian

In contrast to nearly all other atomic and molecular systems, the Schrödinger equation for the one-electron atom can be solved exactly. Because of this, much of our chemical intuition—not only for many-electron atoms, but also molecules—is based on the one-electron, or “hydrogenic” atom. It is important to understand this system thoroughly, as the principles involved arise time and time again.

We start by making the Born-Oppenheimer approximation. The electronic Hamiltonian for the 1-electron atom is seen, from Eq. (1.20) to be equal to

$$\hat{H}_{1\text{el.}} \equiv -\frac{\nabla_{\mathbf{r}}^2}{2} - \frac{Z}{|\mathbf{r} - \mathbf{R}|} \quad (2.1)$$

where \mathbf{r} is the position of the electron, \mathbf{R} is the position of the nucleus, and Z is the atomic number (= nuclear charge). Choosing the atomic nucleus to be located at the origin ($\mathbf{R} = \mathbf{0}$), we may write the Schrödinger equation for the one-electron atom as

$$\begin{aligned} \hat{H}_{1\text{el.}} \Psi(\mathbf{r}) &= E\Psi(\mathbf{r}) \\ \left(-\frac{\nabla^2}{2} - \frac{Z}{|\mathbf{r}|} \right) \Psi(\mathbf{r}) &= E\Psi(\mathbf{r}) \\ \left(-\frac{\nabla^2}{2} - \frac{Z}{r} \right) \Psi(\mathbf{r}) &= E\Psi(\mathbf{r}) \end{aligned} \quad (2.2)$$

B. Separation of Radial and Angular Variables

The electron-nuclear attraction potential is spherically symmetric, which suggests that a transformation to spherical coordinates will be useful. Inserting the Laplacian operator in spherical coordinates, we have

$$\left(-\frac{1}{2} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{Z}{r} \right) \Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (2.3)$$

Recalling from the treatment of the rigid rotor that the operator for the square magnitude of the angular momentum, $\hat{L}^2(\theta, \phi)$ is given by

$$\begin{aligned} \hat{L}^2 &\equiv -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \\ &\xrightarrow{\text{atomic units}} - \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \end{aligned} \quad (2.4)$$

we can rewrite Eq. (2.3) as

$$\left(-\frac{1}{2} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2(\theta, \phi)}{r^2} \right) - \frac{Z}{r} \right) \Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (2.5)$$

Now we use separation of variables. We write $\Psi(\mathbf{r})$ as a product of a radial component, $R_{n,l}(r)$ and an angular component, $\Theta_{l,m}(\theta, \phi)$,

$$\Psi_{n,l,m}(\mathbf{r}) \equiv R_{n,l}(r)\Theta_{l,m}(\theta, \phi). \quad (2.6)$$

Substituting into Eq. (2.5), we obtain,

$$\left(-\frac{1}{2} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2(\theta, \phi)}{r^2} \right) - \frac{Z}{r} \right) R_{n,l}(r)\Theta_{l,m}(\theta, \phi) = E_{n,l,m} R_{n,l}(r)\Theta_{l,m}(\theta, \phi)$$

$$\left(-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Z}{r} + \frac{\hat{L}^2(\theta, \phi)}{2r^2} \right) R_{n,l}(r)\Theta_{l,m}(\theta, \phi) = E_{n,l,m} R_{n,l}(r)\Theta_{l,m}(\theta, \phi) \quad (2.7)$$

$$\left(\Theta_{l,m}(\theta, \phi) \left[-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Z}{r} \right] R_{n,l}(r) + R_{n,l}(r) \frac{\hat{L}^2(\theta, \phi)}{2r^2} \Theta_{l,m}(\theta, \phi) \right) = E_{n,l,m} R_{n,l}(r)\Theta_{l,m}(\theta, \phi)$$

Here we have used the fact that the radial component of the gradient does not effect the angular coordinates, while the angular component of the gradient is a simple multiplicative operator with respect to the radial coordinates.

Now we remember that the eigenfunctions of the rigid rotor are the spherical harmonics, that is,

$$\hat{L}^2(\theta, \phi) Y_l^m(\theta, \phi) = \frac{\hbar^2}{m} l(l+1) Y_l^m(\theta, \phi)$$

$$\xrightarrow{\text{atomic units}} l(l+1) Y_l^m(\theta, \phi), \quad (2.8)$$

which allows us to identify the angular component of the wave function with the spherical harmonics,

$$\Theta_{l,m}(\theta, \phi) = Y_l^m(\theta, \phi). \quad (2.9)$$

Substitution of Eqs. (2.9) and (2.8) into Eq. (2.7) gives

$$\left(Y_l^m(\theta, \phi) \left[-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Z}{r} \right] R_{n,l}(r) + R_{n,l}(r) \frac{\hat{L}^2(\theta, \phi)}{2r^2} Y_l^m(\theta, \phi) \right) = E_{n,l,m} R_{n,l}(r) Y_l^m(\theta, \phi)$$

$$\left(Y_l^m(\theta, \phi) \left[-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Z}{r} \right] R_{n,l}(r) + R_{n,l}(r) \frac{l(l+1)}{2r^2} Y_l^m(\theta, \phi) \right) = E_{n,l,m} R_{n,l}(r) Y_l^m(\theta, \phi) \quad (2.10)$$

$$\left(\left[-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Z}{r} \right] R_{n,l}(r) + R_{n,l}(r) \frac{l(l+1)}{2r^2} \right) = E_{n,l,m} R_{n,l}(r)$$

$$\left(-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) R_{n,l}(r) = E_{n,l} R_{n,l}(r).$$

The last line of Eq. (2.10) is called the radial Schrödinger equation for the hydrogenic atom. In terms of the solutions to this radial equation, the eigenfunctions of the hydrogenic atom are

$$\psi_{n,l,m}(\mathbf{r}) \equiv R_{n,l}(r) Y_l^m(\theta, \phi) \quad (2.11)$$

C. The Radial Schrödinger Equation for the Hydrogenic Atom

Before we continue further, we should comment on the form of the radial Schrödinger equation:

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{l(l+1)}{2r^2}-\frac{Z}{r}\right)R_{n,l}(r)=E_{n,l}R_{n,l}(r) \quad (2.12)$$

- It is important to note that the energy does not depend on azimuthal (or magnetic) quantum number, m . This follows from the fact that there is no m dependence in the “radial Hamiltonian” in Eq. (2.10), which in turn follows from the fact that $\hat{L}^2 Y_l^m(\theta, \phi)$ ($=l(l+1)Y_l^m(\theta, \phi)$) does not depend on m .
- When $l > 0$ there is a repulsive centrifugal potential, $\frac{l(l+1)}{2r^2}$. In physical terms, this potential reflects the fact that it is very difficult (it takes a huge centripetal force) to keep a particle with mass m in a “close” orbit when the magnitude of the orbital angular momentum is $l(l+1)$. In fact, this is just the classical result. We remember from elementary physics that

$$F_{\text{centrifugal}} = \frac{mv^2}{r} \hat{r} \quad (2.13)$$

(\hat{r} is the unit vector in the radial direction) and if we use the fact that $|\mathbf{L}| = |\mathbf{r} \times m\mathbf{v}| = m|\mathbf{r}||\mathbf{v}|\sin(\theta) = mrv$ for circular motion, we can write

$$F_{\text{centrifugal}} = \frac{|\mathbf{L}|^2}{mr^3} \hat{r} \quad (2.14)$$

as the force required to keep a particle of mass m in an orbit whose angular momentum squared is $|\mathbf{L}|^2$ in an orbit with radius r . Since $\mathbf{F} = -\nabla V \rightarrow -\frac{\partial V(r)}{\partial r}$, $V_{\text{centripetal}}(r) = \frac{\mathbf{L} \cdot \mathbf{L}}{2mr^2}$, which is precisely Eq. (2.7). The take-home message is this: for a given angular momentum, the force required to keep a particle in an orbital with radius r increases very rapidly as r decreases toward zero. It should be no surprise that electrons with non-zero orbital angular momentum are never observed at the nucleus.

- The potential is negative everywhere for $l=0$, and is negative except in the immediate vicinity of the nucleus for $l > 0$. Specifically, if

$$r > \frac{l(l+1)}{2Z} \quad (2.15)$$

then the potential energy is negative. This means that the energy levels of the one-electron atom may be separated into two classes. First, those with negative energy ($E < 0$) are “bound states”—they correspond to “stationary states” of the hydrogenic atom. For $E \geq 0$, we have “free electrons”—the electron is no longer confined by the nucleus, and the system can be considered to consist of an electron that is “scattering” off the nucleus. This is very similar to the one-dimension well of finite depth you have already seen: when the energy of a particle is less than the “top” of the well, the particle is bound; otherwise the particle is “free.” We do not worry about the free electrons very much in this course because, chemically speaking, these states can always be thought of as a state of the cation (in this case, the bare nucleus) plus a free electron. You will also recall from the finite well that the energy can only have certain “quantized” values when the energy is less than the height of the well, but that when the energy is greater than the top of the well, the energy can have any value. This, again, is physically reasonable: the energy value of a “free electron” is not constrained by a potential that does not confine it.

We can draw the eigenenergies and wave functions for the one-electron atom in a “schematic” representation reminiscent of the treatment of the harmonic oscillator, particle in a box, etc.. Cf. figures 2.1 and 2.2.

- Very far from the nucleus, the potential is essentially zero. Moreover, the potential is very flat because

$$\begin{aligned} \frac{dV}{dr} &= \frac{dV_{\text{centrifugal}}}{dr} + \frac{dV_{\text{nucleus-electron}}}{dr} \\ &= -\frac{l(l+1)}{r^3} + \frac{Z}{r^2} \end{aligned} \quad (2.16)$$

is very small (much smaller than the potential) at large r . That is, we will make only a very tiny error if we assume that if $R \gg 1$ is a very large number, then for all $r > R$, $V(r) = 0$.

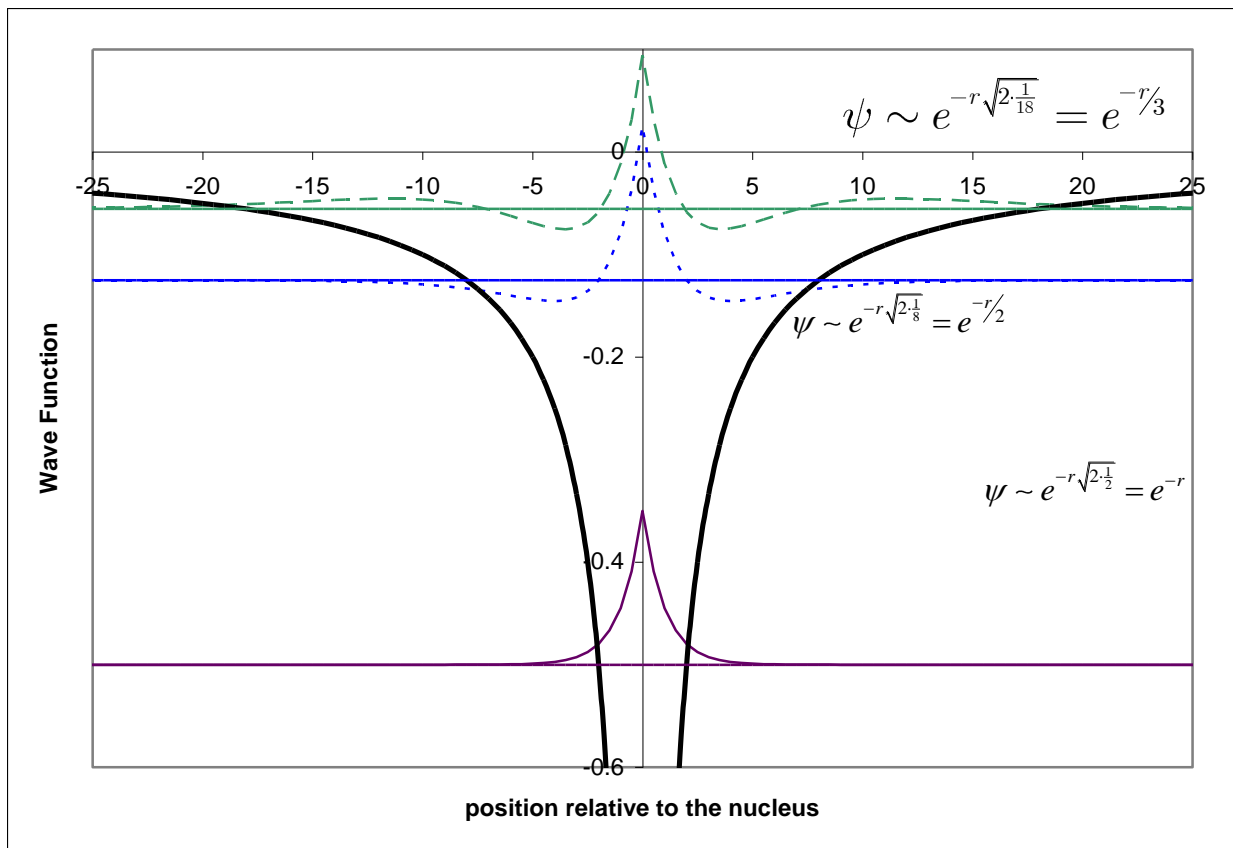


Figure 2.1: Sketch of energy levels and wave functions for the one-electron atom. The heavy black line is the potential, $V(r) = -\frac{Z}{r}$, that binds the electron. The wave functions are plotted so that their “baseline” (which is drawn in the figure) indicates the energy level. The amplitude of the wave functions is chosen so that the plot looks pretty and, in particular, so that wave functions don’t “cross” each other. This sort of plot is useful for visualizing how the shape of the electronic wave function depends on its energy and the potential that confines the electron.

- The following is a very general (and very useful) result: suppose we have a particle of energy E that is confined by a potential whose value at infinity is V_∞ :

$$\lim_{r \rightarrow \infty} V(r) = V_\infty \quad (2.17)$$

For example, for the hydrogenic atom $V_\infty = 0$ and for a particle in a well, $V_\infty = V_{top}$, the potential at the “top” of the well. Then, very far from the system, the wave functions for a state with energy E decays according to the law¹

$$\psi(r) \xrightarrow{\text{large } r} e^{-r \sqrt{\frac{2m}{\hbar^2}(V_\infty - E)}} \quad (2.18)$$

I have written this in 3-dimensions (using $r \equiv |\mathbf{r}|$), but the same result holds in any number of dimensions. Introducing atomic units, we have that wave functions are asymptotically similar to

$$\psi(r) \sim e^{-(\sqrt{2(V_\infty - E)})r} \quad \text{large } r \quad (2.19)$$

In particular, for a “bound state”, $E < V_\infty$ and so the wave function dies off exponentially fast.

$$\psi(r) \sim e^{-(\sqrt{2\alpha^2})r} \quad \text{large } r \quad (2.20)$$

Here, $\alpha \equiv \sqrt{V_\infty - E}$ was defined to emphasize the fact that the exponent is real. For continuum states, $E > V_\infty$ and so the exponent is imaginary:

$$\begin{aligned} \psi(r) &\sim e^{-(\sqrt{2(V_\infty - E)})r} \quad \text{large } r \\ &\sim e^{-i(\sqrt{2(E - V_\infty)})r} \\ &\sim \cos\left(\sqrt{2(E - V_\infty)} \cdot r\right) - i \sin\left(\sqrt{2(E - V_\infty)} \cdot r\right) \end{aligned} \quad (2.21)$$

That is, for continuum states the wave function at long range resembles a periodic function, which is precisely the wave function of a free particle.

¹ A subtle point is that if the potential does not fall off quickly enough at long range, this result does not hold. Fortunately, our potential decays as $\frac{1}{r}$, which is fast enough: if the potential fell off more slowly than this, then matters would be more complicated (although not insurmountably difficult).

$$\psi \sim e^{-r\sqrt{2.204}}$$

States in a Square Well

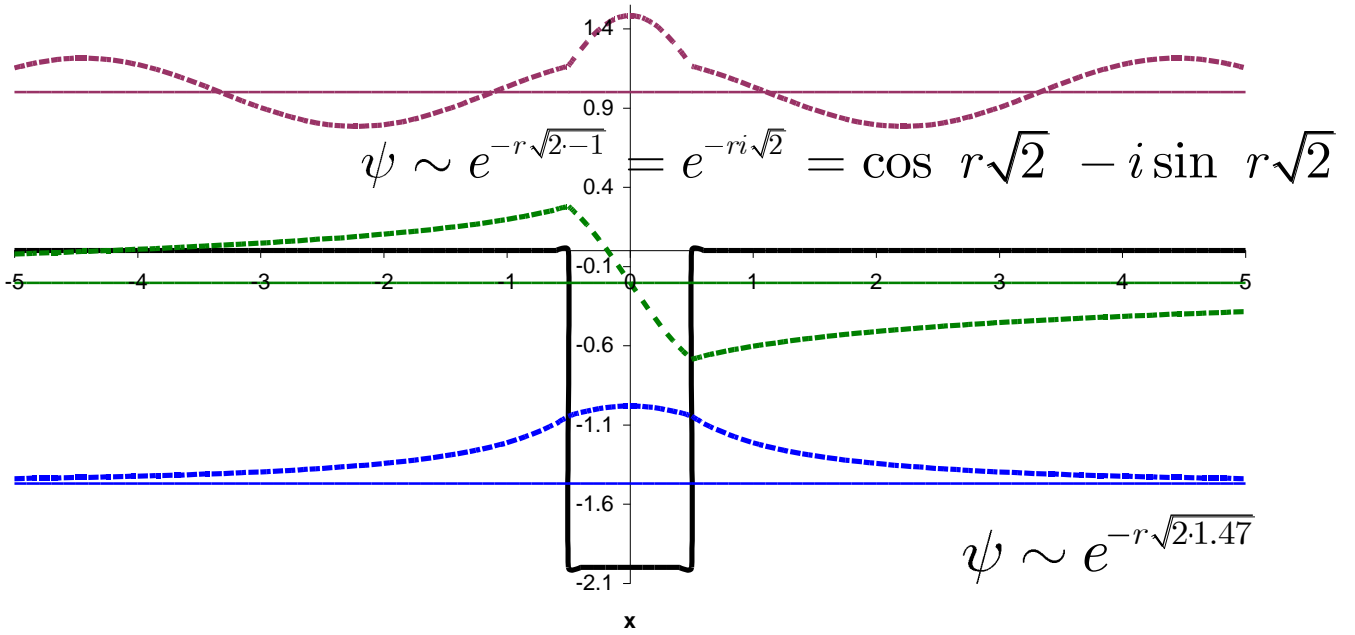


Figure 2.2: Sketch of energy levels and wave functions for an electron in a square well. The equations give the asymptotic (large r) forms for the wave functions. The heavy black line is the potential that binds the electron. The wave functions are plotted so that their “baseline” (which is drawn in the figure) indicates the energy level.

II. Energy Levels and Wave Functions for Hydrogenic Atoms

A. The Ground-State Energy

We now want to derive energy formulae for the one-electron atom. There are several ways to do this, ranging from quite rigorous (see the references posted on the web site) to quite intuitive. The most important thing at this level is to *understand* the one-electron atom, and so we’ll take an intuitive approach. Let’s substitute the asymptotic form for the wave function,

$$\begin{aligned} \psi(r) &\sim e^{-\sqrt{2(V_\infty - E)}r} \\ &\sim e^{-\sqrt{-2E}r} \end{aligned} \quad \left\{ V_\infty = 0 \text{ for the one-electron atom} \right. \quad (2.22)$$

into Eq. (2.12). We have

$$\begin{aligned} &\left(-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) e^{-\sqrt{-2E}r} = E_{n,l} \cdot e^{-\sqrt{-2E}r} \\ &\left(-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial e^{-\sqrt{-2E}r}}{\partial r} \right) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) e^{-\sqrt{-2E}r} = E_{n,l} \cdot e^{-\sqrt{-2E}r} \end{aligned} \quad (2.23)$$

In evaluating the kinetic energy, it is useful to use the identity

$$\begin{aligned}\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} &= \frac{r^2}{r^2} \frac{\partial^2}{\partial r^2} + \frac{2r}{r^2} \frac{\partial}{\partial r} \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}.\end{aligned}\tag{2.24}$$

Using this identity, Eq. (2.23) becomes:

$$\begin{aligned}-\frac{1}{2} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) e^{-\sqrt{-2E}r} + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) e^{-\sqrt{-2E}r} &= E_{n,l} \cdot e^{-\sqrt{-2E}r} \\ -\frac{1}{2} \left((-\sqrt{-2E})^2 e^{-\sqrt{-2E}r} + \frac{2(-\sqrt{-2E})}{r} e^{-\sqrt{-2E}r} \right) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) e^{-\sqrt{-2E}r} &= E_{n,l} \cdot e^{-\sqrt{-2E}r} \\ -\frac{1}{2} \left((-2E) + \frac{-2\sqrt{-2E}}{r} \right) e^{-\sqrt{-2E}r} + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) e^{-\sqrt{-2E}r} &= E_{n,l} \cdot e^{-\sqrt{-2E}r} \\ \left(E + \frac{\sqrt{-2E}}{r} \right) e^{-\sqrt{-2E}r} + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) e^{-\sqrt{-2E}r} &= E_{n,l} \cdot e^{-\sqrt{-2E}r} \\ \left(\frac{l(l+1)}{2r^2} + \frac{\sqrt{-2E}}{r} - \frac{Z}{r} \right) e^{-\sqrt{-2E}r} &= 0 \\ \frac{l(l+1)}{2r^2} + \frac{\sqrt{-2E}}{r} - \frac{Z}{r} &= 0\end{aligned}\tag{2.25}$$

Choosing $l=0$, we obtain an equation for E as a function of Z :

$$\frac{\sqrt{-2E}}{r} - \frac{Z}{r} = 0 \quad \{\text{set } l=0\}\tag{2.26}$$

so that

$$E = \frac{-Z^2}{2}.\tag{2.27}$$

It must be mentioned that we were very lucky: in this case the ground state (1s-orbital) for the Hydrogenic atom is exactly given by the asymptotic form,²

$$\begin{aligned}\Psi_{1,0,0}(\mathbf{r}) &\propto e^{-\sqrt{-2E}r} Y_0^0(\theta, \phi) \\ &\propto e^{-r \sqrt{-2 \left(\frac{-Z^2}{2} \right)}} \\ &\propto e^{-Zr}.\end{aligned}\tag{2.28}$$

How do we know that our solution corresponds to the ground state of the Hydrogen atom and not an excited state? Recall that the eigenfunctions of a Hamiltonian are all orthogonal, so that

$$\int \psi_l(\mathbf{r}) \psi_k(\mathbf{r}) d\mathbf{r} = \delta_{kl}\tag{2.29}$$

² $Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}} = \frac{1}{2\sqrt{\pi}} = \text{constant}$.

where the Kronecker delta, δ_{kl} , is one if $k=l$ and zero otherwise. If $\psi_{n,l,m}(\mathbf{r})$ is any *other* eigenfunction of the Hydrogen atom, then

$$\int \psi_{n,l,m}(\mathbf{r})\psi_{1,0,0}(\mathbf{r})d\mathbf{r} = 0. \quad (2.30)$$

Next, note that $\psi_{1,0,0}(\mathbf{r}) \propto e^{-Zr}$ is always greater than zero. This implies that $\psi_{n,l,m}(\mathbf{r})$ has a node: that is, $\psi_{n,l,m}(\mathbf{r})$ is negative in some places and positive in other places.³ There is a general theorem due to Wintner which indicates that if $\psi_{n,l,m}(\mathbf{r})$ has a node in a region of space where $\psi_{1,0,0}(\mathbf{r})$ does not have a node, then $\psi_{n,l,m}(\mathbf{r})$ is higher in energy.⁴ Since every other wave function of the Hydrogen atom must have a node (otherwise Eq. (2.30) would not be satisfied), $\psi_{1,0,0}(\mathbf{r})$ must be the ground-state eigenfunction and $E = -\frac{Z^2}{2}$ must be the ground-state energy.

B. Energies of States with Non-Zero Angular Momentum ($l > 0$)

We can find out information for the $l > 0$ states by noticing that the centrifugal potential effectively prevents electrons from being close to the nucleus. This suggests that, near the nucleus, $\psi_{l>0}(r) \sim r^\alpha$ ($\alpha > 0$) while, far from the nucleus, the form $\psi(r) \sim e^{-\sqrt{-2E}r}$ must still be valid. The simplest function satisfying both conditions is

$$\psi_{l>0}(r) \sim r^\alpha e^{-\sqrt{-2E}r}. \quad (2.31)$$

Substituting this form into the Schrödinger equation, Eq. (2.12), (we use the form from Eq. (2.24)), we get

³ If this were not true, then $\psi_{n,l,m}(\mathbf{r})\psi_{1,0,0}(\mathbf{r})$ would be either positive everywhere or negative everywhere. If $\psi_{n,l,m}(\mathbf{r})\psi_{1,0,0}(\mathbf{r}) > 0$ for all \mathbf{r} , then

$$\int \psi_{n,l,m}(\mathbf{r})\psi_{1,0,0}(\mathbf{r})d\mathbf{r} = \int [\text{positive function}]d\mathbf{r} > 0$$

If $\psi_{n,l,m}(\mathbf{r})\psi_{1,0,0}(\mathbf{r}) < 0$ for all \mathbf{r} , then

$$\int \psi_{n,l,m}(\mathbf{r})\psi_{1,0,0}(\mathbf{r})d\mathbf{r} = \int [\text{negative function}]d\mathbf{r} < 0$$

Both these cases contradict Eq. (2.30), so it must be that $\psi_{n,l,m}(\mathbf{r})$ is greater than zero in some places and less than zero in other places.

⁴ Recall the wave functions for the particle in a box or, classically, the vibrating string. The lowest-energy eigenfunction had no nodes. The next lowest eigenfunction had one node, at the midpoint of the interval. The next lowest eigenfunction had two nodes, and so forth and so on. (You might look back at Figure 2.2, which shows a similar trend.) Simple stated, the more “wiggles” in the wave function, the higher the energy.

$$\begin{aligned}
& -\frac{1}{2} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) r^\alpha e^{-\sqrt{-2E}r} + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) r^\alpha e^{-\sqrt{-2E}r} = E_{n,l} \cdot r^\alpha e^{-\sqrt{-2E}r} \\
& -\frac{1}{2} \left(\frac{\partial \left[\alpha r^{\alpha-1} e^{-\sqrt{-2E}r} - \sqrt{-2E} r^\alpha e^{-\sqrt{-2E}r} \right]}{\partial r} \right. \\
& \quad \left. + \frac{2}{r} \left[\alpha r^{\alpha-1} e^{-\sqrt{-2E}r} - \sqrt{-2E} r^\alpha e^{-\sqrt{-2E}r} \right] \right) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) r^\alpha e^{-\sqrt{-2E}r} = E_{n,l} \cdot r^\alpha e^{-\sqrt{-2E}r} \\
& -\frac{1}{2} \left(\frac{\partial \left[\alpha(\alpha-1) r^{\alpha-2} e^{-\sqrt{-2E}r} - \alpha \sqrt{-2E} r^{\alpha-1} e^{-\sqrt{-2E}r} \right]}{\partial r} \right. \\
& \quad \left. - \left[\alpha r^{\alpha-1} \sqrt{-2E} e^{-\sqrt{-2E}r} - (\sqrt{-2E})^2 r^\alpha e^{-\sqrt{-2E}r} \right] \right. \\
& \quad \left. + 2\alpha r^{\alpha-2} e^{-\sqrt{-2E}r} - 2\sqrt{-2E} r^{\alpha-1} e^{-\sqrt{-2E}r} \right) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) r^\alpha e^{-\sqrt{-2E}r} = E_{n,l} \cdot r^\alpha e^{-\sqrt{-2E}r} \\
& -\frac{r^\alpha e^{-\sqrt{-2E}r}}{2} \left(\frac{\partial \left[\frac{\alpha(\alpha-1)}{r^2} - \frac{\alpha \sqrt{-2E}}{r} \right]}{\partial r} \right. \\
& \quad \left. - \left[\frac{\alpha}{r} \sqrt{-2E} + (2E) \right] \right. \\
& \quad \left. + \frac{2\alpha}{r^2} - \frac{2\sqrt{-2E}}{r} \right) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) r^\alpha e^{-\sqrt{-2E}r} = E_{n,l} \cdot r^\alpha e^{-\sqrt{-2E}r} \\
& -\frac{1}{2} \left(\left[\frac{\alpha(\alpha-1)+2\alpha}{r^2} - \frac{(2\alpha+2)\sqrt{-2E}}{r} \right] - 2E \right) + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) = E_{n,l} \\
& \quad \left[-\frac{\alpha(\alpha-1)+2\alpha}{2r^2} - \frac{(\alpha+1)\sqrt{-2E}}{2r} \right] + E + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) = E_{n,l} \tag{2.32} \\
& \quad \left[-\frac{\alpha^2+\alpha}{2r^2} + \frac{(\alpha+1)\sqrt{-2E}}{2r} \right] + \left(\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) = 0 \\
& \quad \frac{l(l+1)-\alpha(\alpha+1)}{2r^2} + \frac{((\alpha+1)\sqrt{-2E}-Z)}{r} = 0
\end{aligned}$$

From this analysis, it follows that

$$\alpha = l \tag{2.33}$$

and

$$E = \frac{Z^2}{-2(l+1)^2}. \tag{2.34}$$

Once again, we have been lucky:

$$\begin{aligned}
\psi_{l+1,l,m}(\mathbf{r}) &\propto r^l e^{-\sqrt{2E}r} Y_l^m(\theta, \phi) \\
&\propto r^l e^{-\sqrt{2\left(\frac{Z^2}{-2(l+1)^2}\right)}r} Y_l^m(\theta, \phi) \\
&\propto r^l e^{-\left(\frac{Z}{l+1}\right)r} Y_l^m(\theta, \phi).
\end{aligned} \tag{2.35}$$

Note that Eqs. (2.34) and (2.35) agree with Eqs. (2.27) and (2.28) for the ground state of the hydrogenic atom when $l=0$. This is consistent with the fact that Eqs. (2.34) and (2.35) represent the lowest-energy states with a given value of l .

More generally, we can extend same argument we used in section II.B to show that Eq. (2.35) is the lowest-energy eigenfunction for a given angular momentum. From the orthogonality of eigenfunctions (Eq. (2.29)), we know that

$$\int \psi_{n,l,m}(\mathbf{r}) \psi_{l+1,l,m}(\mathbf{r}) d\mathbf{r} = 0 \tag{2.36}$$

unless $n=l+1$. Separating the wave functions into their angular and radial parts (cf. Eq. (2.11)) and using the fact that the spherical harmonics are normalized, we have that

$$\begin{aligned}
\int \psi_{n,l,m}(\mathbf{r}) \psi_{l+1,l,m}(\mathbf{r}) d\mathbf{r} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} (R_{n,l}(r) Y_l^m(\theta, \phi))^* R_{l+1,l}(r) Y_l^m(\theta, \phi) [r^2 \sin\theta d\phi d\theta dr] \\
&= \int_0^\infty (R_{n,l}(r))^* R_{l+1,l}(r) r^2 \int_0^\pi \int_0^{2\pi} (Y_l^m(\theta, \phi))^* Y_l^m(\theta, \phi) \sin\theta d\phi d\theta dr \\
&= \left[\int_0^\infty (R_{n,l}(r))^* R_{l+1,l}(r) r^2 dr \right] \left[\int_0^\pi \int_0^{2\pi} (Y_l^m(\theta, \phi))^* Y_l^m(\theta, \phi) \sin\theta d\phi d\theta \right] \\
&= \left[\int_0^\infty (R_{n,l}(r))^* R_{l+1,l}(r) r^2 dr \right] [1] \\
&= 0
\end{aligned} \tag{2.37}$$

Note that $R_{l+1,l}(r)r^2$ is always positive. Consequently, $(R_{n,l}(r))^*$ must have both positive and negative values. Since $R_{n,l}(r)$ has “more wiggles” than $R_{l+1,l}(r)$, it will have a higher energy. From this we infer that $\psi_{l+1,l,m}(\mathbf{r})$ is the lowest-energy state with angular momentum l .

If n was less than $l+1$, then we might expect that $\psi_{n,l,m}(\mathbf{r})$ would have a *lower* energy than $\psi_{l+1,l,m}(\mathbf{r})$. The preceding argument shows that this cannot happen, and suggests—but does not prove—that the principle quantum number, n , will always have to be greater than or equal to $l+1$.

C. General Solution to the Hydrogen Atom

Without further ado, we introduce the exact wave functions and energies of the hydrogenic atom. We have

$$E_n = \frac{-Z^2}{2n^2} \tag{2.38}$$

and

$$\Psi_{n,l,m}^S(r, \theta, \phi) \propto \left(\frac{2Zr}{n}\right)^l L_{n-(l+1)}^{2l+1} \left(\frac{2Zr}{n}\right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi). \quad (2.39)$$

Here, $L_{n-(l+1)}^{2l+1}(r)$ are called the associated Laguerre polynomials (sometimes they are called the generalized Laguerre polynomials). They can be defined using the Rodrigues formula,

$$L_m^k(x) = \frac{1}{m!} \frac{e^x}{x^k} \frac{d^m}{dx^m} (x^{m+k} e^{-x}) = \frac{(-1)^k}{(m+k)!} \frac{d^k}{dx^k} \left(e^x \frac{d^{m+k}}{dx^{m+k}} (x^{m+k} e^{-x}) \right) \quad (2.40)$$

I will warn you that this is the standard definition of the Laguerre polynomials.⁵ An alternative definition, popular in the chemistry literature, is

$$\Psi_{n,l,m}^S(r, \theta, \phi) \propto \left(\frac{2Zr}{n}\right)^l \mathcal{L}_{n+l}^{2l+1} \left(\frac{2Zr}{n}\right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \quad (2.41)$$

where

$$\mathcal{L}_m^k(2Zr) = \frac{d^k}{dx^k} \left(e^x \frac{d^m}{dx^m} (x^m e^{-x}) \right) \quad (2.42)$$

The two different definitions are unfortunate, and while the former is to be preferred (being more prevalent and more correct, as it relates directly to Laguerre's studies), the latter form is prevalent in the chemistry literature, to which it was introduced by Linus Pauling and E. Bright Wilson. The main claim for Eq. (2.42) is that it is the definition of the associated Laguerre polynomial definition used by Schrödinger in his first paper. The moral to the story is to make sure you know which definition a given reference is using before plodding ahead.

The associated Laguerre polynomials satisfy the differential equations

$$x \frac{d^2 L_m^k(x)}{dx^2} + (k+1-x) \frac{dL_m^k(x)}{dx} + mL_m^k(x) = 0 \quad (2.43)$$

and

$$x \frac{d^2 \mathcal{L}_m^k(x)}{dx^2} + (k+1-x) \frac{d\mathcal{L}_m^k(x)}{dx} + (k-m)\mathcal{L}_m^k(x) = 0. \quad (2.44)$$

If one substitutes the radial portion of the wave function, $\Psi_{n,l,m}(\mathbf{r})$, into the Schrödinger equation, one can confirm that the Laguerre polynomials solve the Schrödinger equation using Eq. (2.43) or (2.44).

A useful result is an explicit form for the Laguerre polynomials, namely,

$$\begin{aligned} L_m^k(r) &= \sum_{j=0}^m (-1)^j \frac{(m+k)!}{(m-j)!(k+j)!} \frac{x^j}{j!} \\ &= \sum_{j=0}^m (-1)^j \binom{m+k}{m-j} \frac{x^j}{j!} \end{aligned} \quad (2.45)$$

where we have introduced the binomial coefficient,

⁵ In fact, in the physics literature the Laguerre polynomials are usually normalized in a different way; the Laguerre polynomials used by physicists are the proportional to those defined by Eq. (2.40), but multiplied by a factor of $(m+k)!$ (which makes the second Rodriguez formula in Eq. (2.40) a bit simpler).

$$\binom{P}{p} \equiv \frac{P!}{(P-p)!p!} \quad (2.46)$$

Comparing the exact energy formula (Eq. (2.38)) to Eq. (2.34) we identify $l_{\max} = n-1$ as the highest-permissible value for the orbital angular momentum quantum number, l , for a given value of the principle quantum number, n . (If this were not true, then Eq. (2.34) would not be the lowest energy state for a give value of l .)

A more lucid argument uses Eq. (2.45). Writing

$$\begin{aligned} L_{n-l-1}^{2l+1}(r) &= \sum_{j=0}^{n-l-1} (-1)^j \frac{(n-l-1+2l+1)!}{(n-l-1-j)!(2l+1+j)!} \frac{x^j}{j!} \\ &= \sum_{j=0}^{n-l-1} (-1)^j \frac{(n+l)!}{(n-l-j-1)!(2l+1+j)!} \frac{x^j}{j!} \end{aligned} \quad (2.47)$$

The sum does not exist unless $n-l_{\max}-1 \geq 0$. Alternatively, from Eq. (2.40) it is clear that $L_{n-l-1}^{2l+1}(x)$ is a polynomial of degree $n-l-1$, and so the fact a polynomial cannot have negative degree requires $l_{\max} = n-1$.⁶ From the treatment of the rigid rotor, we know that $l=0,1,2,\dots$ and $m=-l,-l+1,\dots,l-1,l$. That $0 \leq l \leq n-1$ can also be deduced from Eq. (2.47): if $l < 0$ or $l > n+1$, there is a negative factorial in the denominator of Eq. (2.47) and $k! = \Gamma(k+1) \rightarrow \pm\infty$ when $k = -1, -2, \dots$.⁷

That $n=1,2,3,\dots$ is revealed from the identity $n=l_{\max}+1$, or, alternatively, from the fact the lowest energy level (cf. Eq. (2.27)) already has $n=1$. There is no $n=0$ state.

D. Qualitative Observations about Hydrogenic Energies and Orbitals

Some notes on the one-electron atom's energy levels and wave functions:

- Note that the energy of the one-electron atom is independent of l and m . This reflects a "hidden symmetry" in momentum space. The important point is that any perturbation of the Coulomb form of the potential will cause the degeneracy of orbitals with different l values to disappear.
- Traditionally hydrogen atom orbitals are labeled as

⁶ Recall that the degree of a polynomial, $P(x)$, is defined as the highest power of x occurring in the polynomial. This, $P(x) = x^2 + 2x^3 + 7x^{13}$ is a polynomial of degree thirteen. More generally, a polynomial of degree d can be written in the form

$$P(x) = \sum_{n=0}^d a_n x^n$$

⁷ The gamma function is defined as the function that has the property

$$\Gamma(x+1) = x\Gamma(x)$$

hence the result that

$$n! = \Gamma(n+1) = n\Gamma(n) = n(n-1)\Gamma(n-2) = n(n-1)(n-2)\cdots(1)\Gamma(1) = n(n-1)(n-2)\cdots(1)(1)$$

$$\begin{aligned}l = 0 &\rightarrow ns \\l = 1 &\rightarrow np \\l = 2 &\rightarrow nd \\l = 3 &\rightarrow nf \\l = 4 &\rightarrow ng \\l = 5 &\rightarrow nh \\&\vdots\end{aligned}\tag{2.48}$$

This is a historical artifact from the fact that the spectral lines from states with $l=0$ are “sharp”, those with $l=1$ are “principle”, those with $l=2$ are “diffuse”, and those with $l=3$ are “fundamental”. At this point, ancient spectroscopists ran out of adjectives and decided to use the alphabet.

- The first few eigenstates of the Hydrogenic atom are plotted in figure 2.3. The equations for the orbitals are listed below.

$$\begin{aligned}
\psi_{1s}(\mathbf{r}) &= \Psi_{1,0,0}(\mathbf{r}) = \sqrt{2^2 Z^3} \cdot e^{-Zr} Y_0^0(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{\pi}} \cdot e^{-Zr} \\
\psi_{2s}(\mathbf{r}) &= \Psi_{2,0,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{2^3}} \cdot (2 - Zr) e^{-Zr/2} Y_0^0(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2^5 \pi}} \cdot (2 - Zr) e^{-Zr/2} \\
\psi_{2p_0}(\mathbf{r}) &= \Psi_{2,1,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{3 \cdot 2^3}} \cdot (Zr) e^{-Zr/2} Y_1^0(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Zr) e^{-Zr/2} \cos(\theta) \\
\psi_{2p_{\pm 1}}(\mathbf{r}) &= \Psi_{2,1,\pm 1}(\mathbf{r}) = \sqrt{\frac{Z^3}{3 \cdot 2^3}} \cdot (Zr) e^{-Zr/2} Y_1^{\pm 1}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2^6 \pi}} \cdot (Zr) e^{-Zr/2} \sin(\theta) e^{\pm i\phi} \\
\psi_{3s}(\mathbf{r}) &= \Psi_{3,0,0}(\mathbf{r}) = \sqrt{\frac{2^2 Z^3}{3^9}} \cdot (27 - 18Zr + 2(Zr)^2) e^{-Zr/3} Y_0^0(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{3^9 \pi}} \cdot (27 - 18Zr + 2(Zr)^2) e^{-Zr/3} \\
\psi_{3p_0}(\mathbf{r}) &= \Psi_{3,1,0}(\mathbf{r}) = \sqrt{\frac{2^3 Z^3}{3^9}} \cdot (Zr)(6 - Zr) e^{-Zr/3} Y_1^0(\theta, \phi) \\
&= \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Zr)(6 - Zr) e^{-Zr/3} \cos(\theta) \\
\psi_{3p_{\pm 1}}(\mathbf{r}) &= \Psi_{3,1,\pm 1}(\mathbf{r}) = \sqrt{\frac{2^3 Z^3}{3^9}} \cdot (Zr)(6 - Zr) e^{-Zr/3} Y_1^{\pm 1}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{3^8 \pi}} \cdot (Zr)(6 - Zr) e^{-Zr/3} \sin(\theta) e^{\pm i\phi}
\end{aligned} \tag{2.49}$$

$$\begin{aligned}
\psi_{3d_0}(\mathbf{r}) &= \Psi_{3,2,0}(\mathbf{r}) = \sqrt{\frac{2^3 Z^3}{3^9 \cdot 5}} \cdot (Zr)^2 e^{-Zr/3} Y_1^0(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2 \cdot 3^9 \pi}} \cdot (Zr)^2 e^{-Zr/3} (3 \cos^2(\theta) - 1) \\
\psi_{3d_{\pm 1}}(\mathbf{r}) &= \Psi_{3,2,\pm 1}(\mathbf{r}) = \sqrt{\frac{2^3 Z^3}{3^9 \cdot 5}} \cdot (Zr)^2 e^{-Zr/3} Y_1^{\pm 1}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{3^8 \pi}} \cdot (Zr)^2 e^{-Zr/3} \sin(\theta) \cos(\theta) e^{\pm i\phi} \\
\psi_{3d_{\pm 2}}(\mathbf{r}) &= \Psi_{3,2,\pm 2}(\mathbf{r}) = \sqrt{\frac{2^3 Z^3}{3^9 \cdot 5}} \cdot (Zr)^2 e^{-Zr/3} Y_1^{\pm 2}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2^2 \cdot 3^8 \pi}} \cdot (Zr)^2 e^{-Zr/3} \sin^2(\theta) e^{\pm 2i\phi}
\end{aligned} \tag{2.50}$$

Hydrogenic Orbitals (n=1)

— PSI1s(r) — P1s(r)

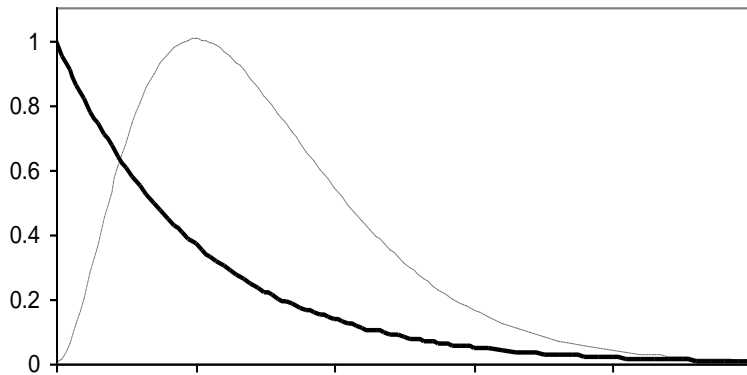


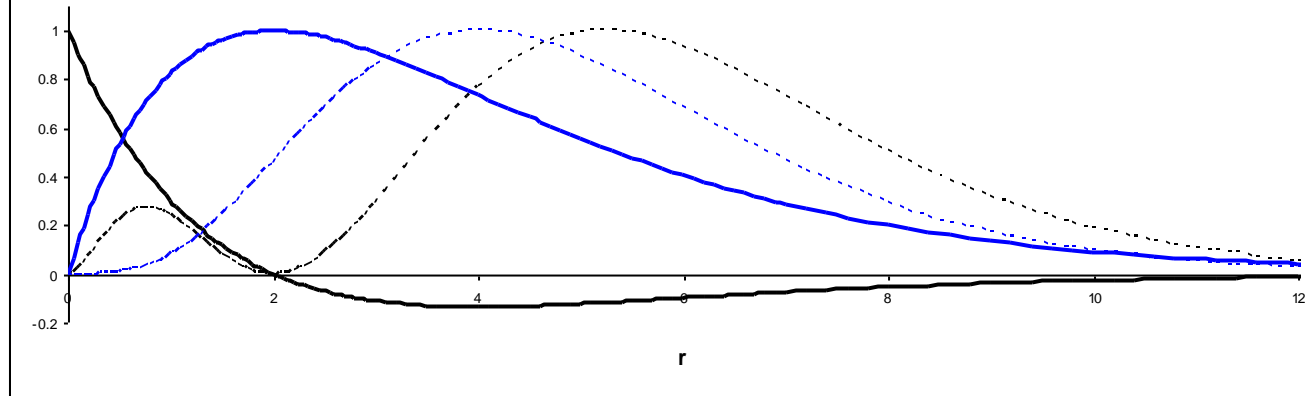
Figure 2.3. Radial wave functions, $\psi_{nl}(r)$, and radial probability distribution functions,

$$P_{nl}(r) = \int_0^\pi \int_0^{2\pi} |\psi(r)|^2 r^2 \sin(\theta) d\phi d\theta,$$

for Hydrogenic states with various principle quantum numbers. For convenience when plotting, the wave functions and probabilities are not normalized.

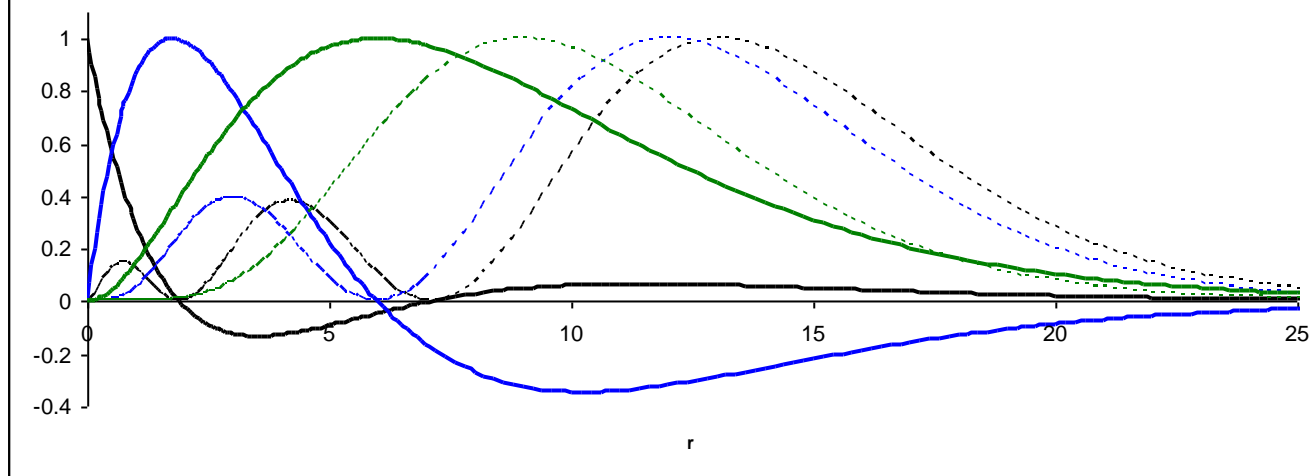
Hydrogenic orbitals (n=2)

— PSI2s(r) - - - P2s(r) — PSI2p(r) - · - · P2p(r)



Hydrogenic Orbitals (n=3)

— PSI3s(r) - - - P3s(r) — PSI3p(r) - · - · P3p(r) — PSI3d(r) - · - · P3d(r)



- One important point is that the “nodes” of the orbitals—the places where $(L_{n-l-1}^{2l+1}(r) = 0 \rightarrow \Psi_{n,l,m}(r, \theta, \phi) = 0)$ are interleaved (some people say interlaced). That is, given an ns orbital, the position of the first node is before the first node in the $(n-1)s$ orbital, the second node is after the first node in the $(n-1)s$ orbital but before the second, and so forth. If we label the nodes in the radial component of the wave function, $R_{n,l}(r)$, with $\mathcal{R}_i(n,l)$ where $\mathcal{R}_0(n,l)$ is the first node and $\mathcal{R}_{n-l-1}(n,l)$ is the last node, we have that $\mathcal{R}_0(n,l) < \mathcal{R}_0(n-1,l) < \mathcal{R}_1(n,l) < \mathcal{R}_1(n-1,l) < \dots < \mathcal{R}_{n-l-2}(n-1,l) < \mathcal{R}_{n-l-1}(n,l)$ (2.51)

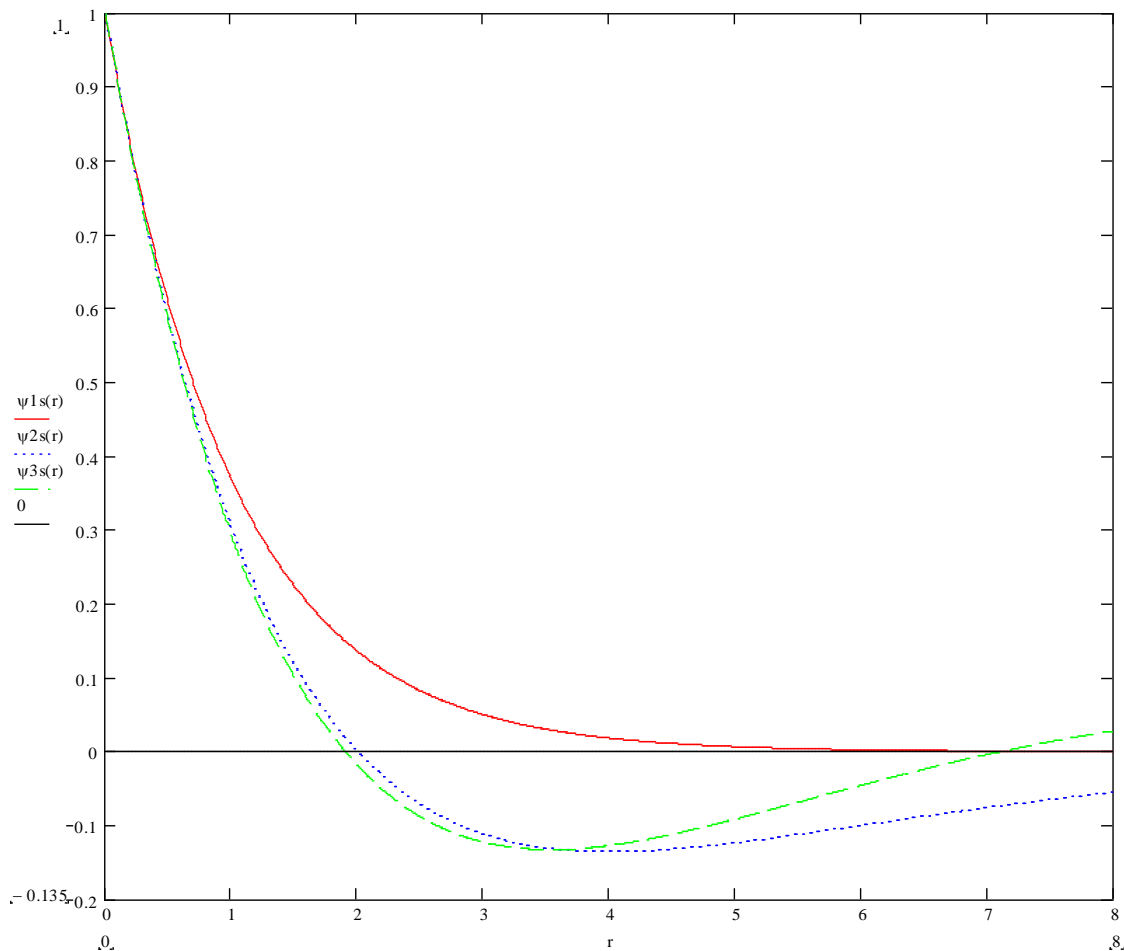


Figure 2.3. The 1s, 2s, and 3s wave function for the Hydrogen atom, showing the interlacing of the nodes. These wave functions are not normalized. The first node in the 3s orbital is before the node in the 2s orbital, and the second node in the 3s orbital is after the node in the 2s orbital. The nodes in the 4s orbital would be before the first node in the 3s orbital, between the two nodes in the 3s orbital, and after the last node in the 3s orbital.

- The angular components of the p and d orbitals above are magnetic eigenstates, and not the “electrostatic” eigenstates you are used to. See the figure 2.4.

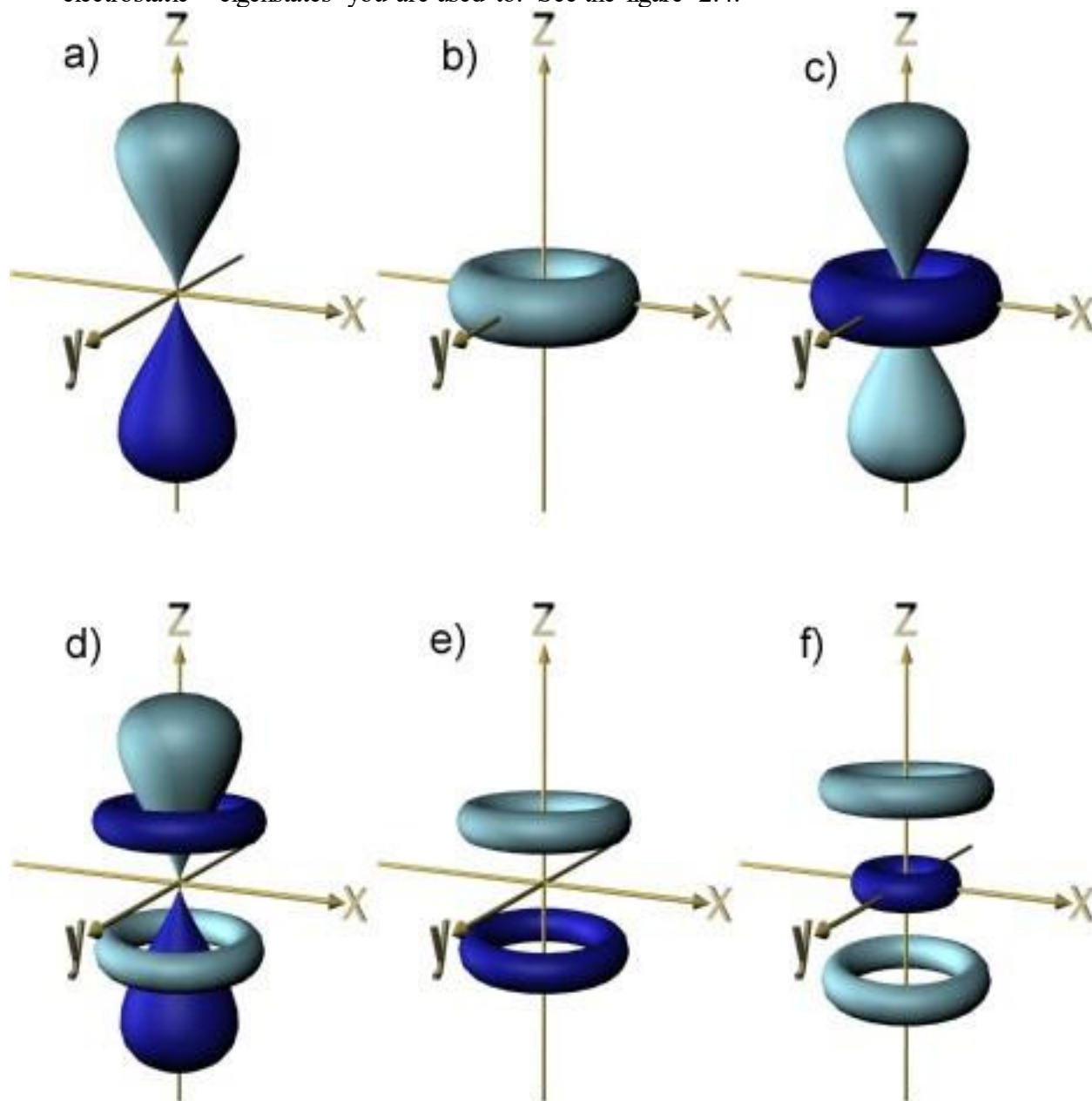


Figure 2.4: The angular part of the wave functions for various values of l and m_l ; only the real part of the wave functions is plotted.

- (a) The $2p_0 = 2p_z$ orbital, $Y_1^0(\theta, \phi)$.
- (b) The $2p_{\pm 1}$, $3d_{\pm 2}$, and $4f_{\pm 3}$ orbitals have this general shape; $Y_l^{\pm l}(\theta, \phi)$.
- (c) The $3d_0 = 3d_{z^2}$ orbital, $Y_2^0(\theta, \phi)$.
- (d) The $4f_0 = 4f_{z^3}$ orbital, $Y_3^0(\theta, \phi)$.
- (e) The $3d_{\pm 1}$ and $4f_{\pm 2}$ orbitals have this general shape; $Y_l^{\pm(l-1)}(\theta, \phi)$.
- (f) The $4f_{\pm 1}$ orbitals have this general shape; $Y_l^{\pm(l-2)}(\theta, \phi)$.

The degeneracy in the orbitals with $|m_l| > 0$ is not apparent from figure 2.4. This is because we've plotted only the "real part" of them, and the $\pm m_l$ orbitals differ only by a "phase" factor about the z axis. The idea is that the electron is orbiting (either clockwise or counterclockwise) around the axis. When the electron is moving in the z -direction, there is no angular momentum about the z -axis. (Said differently, since an electron moving in the z -direction is moving perpendicular to the xy -plane, there will be no angular momentum about the z -axis, though there will generally be angular momentum about the x and y axes.) When the electron is "orbiting" the z -axis, as in the orbitals with $|m_l| > 0$, then there is a component of the electrons momentum about the z axis. If the electron goes from "clockwise rotation" to "counterclockwise rotation", the angular momentum changes sign. In any event, the key is to note that the aforementioned hydrogenic atom wave functions are eigenfunctions of

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad (2.52)$$

since

$$\hat{L}_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi). \quad (2.53)$$

- Often one chooses to use the "real" orbitals, which correspond to the hydrogenic orbitals in electric (rather than magnetic) fields. This gives the conventional "chemistry" orbitals you know by heart. The key is to recall that

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \quad (2.54)$$

and use this, along with some trigonometric identities, to form "Cartesian" orbitals.

A few of the real orbitals are listed below

$$\begin{aligned} \psi_{2p_z}(\mathbf{r}) &= \psi_{2p_0} = \sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Z \cdot z) e^{-Zr/2} \\ \psi_{2p_x}(\mathbf{r}) &= \frac{\psi_{2p_{+1}} + \psi_{2p_{-1}}}{\sqrt{2}} = \left(\sqrt{\frac{Z^3}{2^6 \pi}} \cdot (Z) e^{-Zr/2} \right) r \sin \theta (\sqrt{2}) \left(\frac{e^{+i\phi} + e^{-i\phi}}{2} \right) \\ &= \left(\sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Z) e^{-Zr/2} \right) r \sin \theta \cos(\phi) = \left(\sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Z \cdot x) e^{-Zr/2} \right) \\ \psi_{2p_y}(\mathbf{r}) &= \frac{\psi_{2p_{+1}} - \psi_{2p_{-1}}}{i\sqrt{2}} = \left(\sqrt{\frac{Z^3}{2^6 \pi}} \cdot (Z) e^{-Zr/2} \right) r \sin \theta (\sqrt{2}) \left(\frac{e^{+i\phi} - e^{-i\phi}}{2i} \right) \\ &= \left(\sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Z) e^{-Zr/2} \right) r \sin \theta \sin(\phi) = \left(\sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Z \cdot y) e^{-Zr/2} \right) \end{aligned} \quad (2.55)$$

$$\begin{aligned}
\psi_{3d_{2z^2-x^2-y^2}}(\mathbf{r}) &= \psi_{3d_{3z^2-r^2}}(\mathbf{r}) = \psi_{3d_{z^2}}(\mathbf{r}) = \psi_{3d_0}(\mathbf{r}) = \sqrt{\frac{Z^3}{2 \cdot 3^9 \pi}} \cdot (Z)^2 e^{-Zr/3} (3r^2 \cos^2(\theta) - r^2) \\
&= \sqrt{\frac{Z^3}{2 \cdot 3^9 \pi}} \cdot (Z)^2 e^{-Zr/3} (3z^2 - r^2) = \sqrt{\frac{Z^3}{2 \cdot 3^9 \pi}} \cdot (Z)^2 e^{-Zr/3} (3z^2 - (x^2 + y^2 + z^2)) \\
&= \sqrt{\frac{Z^3}{2 \cdot 3^9 \pi}} \cdot (Z)^2 e^{-Zr/3} (2z^2 - x^2 - y^2) \\
\psi_{3d_{xz}}(\mathbf{r}) &= \frac{\psi_{3d_1}(\mathbf{r}) + \psi_{3d_{-1}}(\mathbf{r})}{\sqrt{2}} = \sqrt{\frac{Z^3}{3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} (r^2 \sin(\theta) \cos(\theta)) \sqrt{2} \left(\frac{e^{+i\phi} + e^{-i\phi}}{2} \right) \\
&= \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} (r \cos(\theta))(r \sin(\theta) \cos(\phi)) = \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} \cdot xz \\
\psi_{3d_{xy}}(\mathbf{r}) &= \frac{\psi_{3d_1}(\mathbf{r}) - \psi_{3d_{-1}}(\mathbf{r})}{i\sqrt{2}} = \sqrt{\frac{Z^3}{3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} (r^2 \sin(\theta) \cos(\theta)) \sqrt{2} \left(\frac{e^{+i\phi} - e^{-i\phi}}{2i} \right) \\
&= \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} (r \cos(\theta))(r \sin(\theta) \sin(\phi)) = \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} \cdot xy \\
\psi_{3d_{x^2-y^2}}(\mathbf{r}) &= \frac{\psi_{3d_2}(\mathbf{r}) + \psi_{3d_{-2}}(\mathbf{r})}{\sqrt{2}} = \sqrt{\frac{Z^3}{4 \cdot 3^8 \pi}} \cdot (Zr)^2 e^{-Zr/3} \sin^2(\theta) \sqrt{2} \left(\frac{e^{+2i\phi} + e^{-2i\phi}}{2} \right) \\
&= \sqrt{\frac{Z^3}{2 \cdot 3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} r^2 \sin^2(\theta) \cos(2\phi) \\
&= \sqrt{\frac{Z^3}{2 \cdot 3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} r^2 \sin^2(\theta) (\cos^2(\phi) - \sin^2(\phi)) = \sqrt{\frac{Z^3}{2 \cdot 3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} (x^2 - y^2) \\
\psi_{3d_{yz}}(\mathbf{r}) &= \frac{\psi_{3d_2}(\mathbf{r}) - \psi_{3d_{-2}}(\mathbf{r})}{i\sqrt{2}} = \sqrt{\frac{Z^3}{4 \cdot 3^8 \pi}} \cdot (Zr)^2 e^{-Zr/3} \sin^2(\theta) \sqrt{2} \left(\frac{e^{+2i\phi} - e^{-2i\phi}}{2i} \right) \\
&= \sqrt{\frac{Z^3}{2 \cdot 3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} r^2 \sin^2(\theta) \sin(2\phi) = \sqrt{\frac{Z^3}{2 \cdot 3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} r^2 \sin^2(\theta) (2 \cos(\phi) \sin(\phi)) \\
&= \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Z)^2 e^{-Zr/3} (xz)
\end{aligned} \tag{2.56}$$

The moral to the story is this: a ‘‘Cartesian’’ orbital is an eigenfunction of \hat{L}_z only if its coordinate dependences can be written entirely in terms of z and r^2 . This is because an electron moving in the z direction has no angular momentum about the z -axis, and $\hat{L}_z f(r) = 0$, where $f(r)$ is a spherically symmetric function. Combining the two rules, we see that

$$\hat{L}_z f(z, r) = 0 \tag{2.57}$$

and that the only eigenstate of \hat{L}_z that is also a Cartesian eigenstate is $Y_l^0(\theta, \phi)$.

III. Epilogue

A. Hydrogenic Atoms: SI Units

It is important to be able to “reintroduce” the SI units for the energy. For the hydrogenic atom, there is an easy way to extract the dependence of the energy on other parameters, e.g., the mass of the particle. Write the Schrödinger equation for the one-electron atom in SI units,

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right) \Psi_n(\mathbf{r}) = E_n \Psi_n(\mathbf{r}) \quad (2.58)$$

Multiply both sides by $\frac{m_e}{\hbar^2}$. Then

$$\left(-\frac{1}{2} \nabla^2 - \frac{Ze^2 m_e}{4\pi\epsilon_0 \hbar^2 r} \right) \Psi_n(\mathbf{r}) = \frac{m_e}{\hbar^2} E_n \Psi_n(\mathbf{r}). \quad (2.59)$$

Equation (2.59) is the Schrödinger equation for a one-electron atom with atomic number

$$Z_{\text{eff}} = \frac{Ze^2 m_e}{4\pi\epsilon_0 \hbar^2}. \quad (2.60)$$

The Schrödinger equation, Eq. (2.59), can then be rewritten as

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z_{\text{eff}}}{r} \right) \Psi_n(\mathbf{r}) = \left(-\frac{Z_{\text{eff}}^2}{2n^2} \right) \Psi_n(\mathbf{r}). \quad (2.61)$$

Equating the right-hand-sides of Eqs. (2.59) and (2.61)

$$\frac{m_e}{\hbar^2} E_n \Psi(\mathbf{r}) = \frac{-Z_{\text{eff}}^2}{2n^2} \Psi(\mathbf{r}) \quad (2.62)$$

Then, from the definition of Z_{eff} (Eq. (2.60)),

$$\begin{aligned} E_n &= \frac{\hbar^2}{m_e} \left(\frac{Ze^2 m_e}{4\pi\epsilon_0 \hbar^2} \right)^2 \\ &= - \left(\frac{Z^2}{2n^2} \right) \left(\frac{e^4 m_e}{(4\pi\epsilon_0)^2 \hbar^2} \right). \end{aligned} \quad (2.63)$$

B. The Hellmann-Feynman Theorem

The dependence of the energy on the angular momentum was derived using asymptotic analysis in Eq. (2.32). A simpler (but less rigorous) approach uses the Hellmann-Feynman theorem.

Hellmann-Feynman Theorem: Suppose the Hamiltonian $\hat{H}(\lambda)$ depends on a parameter λ .

Then the dependence of the energy of an eigenstate of the Hamiltonian, Ψ , on the parameter λ is given by

$$\frac{\partial E}{\partial \lambda} \equiv \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle. \quad (2.64)$$

Proof:

To derive this result, we differentiate on the definition of the energy,

$$\begin{aligned}
\frac{\partial E[\Psi]}{\partial \lambda} &\equiv \frac{\partial}{\partial \lambda} \int \Psi^*(\tau) \hat{H}(\lambda) \Psi(\tau) d\tau \\
&= \int \frac{\partial}{\partial \lambda} (\Psi^*(\tau) \hat{H}(\lambda) \Psi(\tau)) d\tau \\
&= \int \left[\frac{\partial \Psi^*(\tau)}{\partial \lambda} (\hat{H}(\lambda) \Psi(\tau)) + \frac{\partial \Psi(\tau)}{\partial \lambda} (\Psi^*(\tau) \hat{H}(\lambda)) + \left(\Psi^*(\tau) \left(\frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right) \Psi(\tau) \right) \right] d\tau \\
&= \left\langle \Psi \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \Psi \right\rangle + \int \left[\frac{\partial \Psi^*(\tau)}{\partial \lambda} (E\Psi(\tau)) + \frac{\partial \Psi(\tau)}{\partial \lambda} (\hat{H}(\lambda) \Psi(\tau))^* \right] d\tau \\
&= \left\langle \Psi \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \Psi \right\rangle + \int \left[\frac{\partial \Psi^*(\tau)}{\partial \lambda} (E\Psi(\tau)) + \frac{\partial \Psi(\tau)}{\partial \lambda} (E\Psi(\tau))^* \right] d\tau \\
&= \left\langle \Psi \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \Psi \right\rangle + E \int \left[\frac{\partial \Psi^*(\tau)}{\partial \lambda} \Psi(\tau) + \Psi^*(\tau) \frac{\partial \Psi(\tau)}{\partial \lambda} \right] d\tau \\
&= \left\langle \Psi \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \Psi \right\rangle + E \frac{\partial}{\partial \lambda} \int \Psi^*(\tau) \Psi(\tau) d\tau \\
&= \left\langle \Psi \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \Psi \right\rangle + E \frac{\partial(1)}{\partial \lambda} \\
&= \left\langle \Psi \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \Psi \right\rangle.
\end{aligned} \tag{2.65}$$

Q.E.D

The similarity to first-order perturbation theory is to be expected, since

$$\hat{H}(\lambda + d\lambda) \equiv \hat{H}(\lambda) + \frac{\partial \hat{H}}{\partial \lambda} d\lambda + \dots \tag{2.66}$$

Indeed, this is an easy way to derive perturbation series when the dependence of the Hamiltonian on the “strength” of the perturbation is nonlinear.

As an example, we consider the dependence of the energy on the angular momentum quantum number l in the 1s state. Using Eq. (2.34), we know that the result is

$$\frac{\partial E}{\partial l} = \frac{\partial}{\partial l} \left(\frac{-Z^2}{2(l+1)^2} \right) = -\frac{Z^2(-2)}{2(l+1)^3} = \frac{Z^2}{(l+1)^3} \xrightarrow[l=0]{1s \text{ state}} Z^2. \tag{2.67}$$

But suppose we did not know this result. Then we could evaluate

$$\begin{aligned}
\left. \frac{\partial E}{\partial l} \right|_{l=0} &= \int \Psi_{1s}^*(\mathbf{r}) \left. \frac{\partial \hat{H}}{\partial l} \right|_{l=0} \Psi_{1s}(\mathbf{r}) d\mathbf{r} \\
&= \int \Psi_{1s}^*(\mathbf{r}) \left(\frac{2l+1}{2r^2} \right)_{l=0} \Psi_{1s}(\mathbf{r}) d\mathbf{r} \\
&= \int_0^\infty \sqrt{\frac{Z^3}{\pi}} e^{-Zr} \left(\frac{1}{2r^2} \right) \sqrt{\frac{Z^3}{\pi}} e^{-Zr} \cdot 4\pi r^2 dr \\
&= \frac{Z^3}{\pi} \frac{(4\pi)}{2} \int_0^\infty e^{-2Zr} dr \\
&= 2Z^3 \left(\frac{-1}{2Z} \right) [e^{-2Zr}]_0^\infty \\
&= Z^2
\end{aligned} \tag{2.68}$$

That is, instead of performing the analysis in Eq. (2.32), we could have tried to guess the result using Eq. (2.68). Though there are certainly many forms that are consistent with Eq. (2.68) (just knowing the first derivative of a function is not enough to completely specify its functional form), the desired result, Eq. (2.34), certainly seems to be the simplest such form.

The Hellmann-Feynman theorem can also be used to determine the dependence of the energy on other terms in the Hamiltonian, e.g., Planck's constant, particle mass, or particle charge. You may wish to verify Eq. (2.63) using the Hellmann-Feynman theorem.